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The stabilisation of organic carbon via chemical interactions with Fe and Al oxides in gley soils

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Abstract

The importance of soil organic carbon (SOC) stabilisation via chemical interactions with Fe and Al oxide minerals within gley soils remains unclear. Changes in the proportions of Fe/Al oxides and SOC and N contents associated with Fe/Al oxides within the profiles of gley soils under contrasting hydrological regimes and freely draining control soils from Harwood Forest (northeast England) were investigated. Sequential selective dissolution techniques were used to measure Fe/Al oxide crystallinity and explore whether crystallinity differed between gleyed and freely draining soils. Extracts were analysed using FT-IR spectroscopy to investigate the chemical characteristics of organic matter (OM) associated with Fe/Al oxides. Strongly crystalline Fe oxides were the dominant (~ 50-80 % of total Fe oxides present) mineral phase in gley mineral soils. Contrasting gley soil hydrological regimes influenced total subsoil Fe, and total and weakly crystalline Al oxide concentrations. Also, within-profile changes in strongly crystalline Fe oxide concentrations were linked to differences in hydrological and redox conditions. A large proportion of SOC (generally 70-90 % of total) appeared to be associated with Fe/Al oxides. Correlation plots, however, indicated that SOC contents were not linearly related to amounts of total Fe and Al oxides, weakly crystalline Fe and Al oxides or strongly crystalline Fe oxides. The lack of linear correlations observed for these acidic soils may be due to contributions from other extractable soil components and factors such as high organic loadings and insufficient amounts of Fe/Al oxides for interaction with SOC in topsoils and variable surface loadings of different organic inputs at different soil depths. Subsoil C/N ratios (~18-21) were higher than those in extracted subsoil residues (~9-17), suggesting that minerals other than Fe/Al oxides preferentially adsorbed N-rich microbially processed compounds. The OM associated with weakly and strongly crystalline Fe/Al-oxides was chemically different, the latter generally having greater hydroxyl, aliphatic, carboxylate and/or phenolic character and less carbohydrate character than the former. This research shows that interactions between Fe/Al oxides and SOM in redox-dynamic gley soils under different hydrological regimes are complex and further investigations of SOC stabilisation in these systems using selective dissolution and other complementary techniques are required.

Keywords: Gley soils, soil organic carbon, iron oxides, organo-mineral interactions, oxalate, dithionite

1. Introduction

The formation of stable pools of soil organic carbon (SOC) is a key process in the global terrestrial carbon cycle. Since twice as much carbon is stored in the soil than in the atmosphere (Lal et al. 1995), increasing interest in carbon storage has led to active research into SOC stabilisation. One pathway for the formation of stable SOC, for which the mechanisms are still not fully understood, is via SOC-mineral interactions. Soil organic matter (SOM) preferentially sorbs to metal oxyhydroxides and clay minerals such as smectite (Guggenberger and Kaiser 2003) and the stabilisation of SOM through organo-mineral interactions involving reactive sesquioxide and clay mineral surfaces has been reported in many studies (Kaiser et al. 2002; Eusterhues et al. 2005 a and b; Wiseman and Püttmann 2006; von Lützow et al. 2006; Wagai and Mayer 2007; Kalbitz and Kaiser 2008). Along with plant roots, fungal hyphae and microbial- and plant-derived polysaccharides, weakly crystalline Fe and Al oxides are important aggregate-binding agents (Oades, 1988; D'Angelo et al. 2009) and soil aggregate stability has been found to increase with increasing Fe and Al oxide content (Krull et al. 2003). Weakly crystalline minerals such as ferrihydrite ($Fe_2O_3.0.5H_2O$) and amorphous $Al(OH)_3$ have a high degree of hydration, extensive surface area and variable charge and are thought to form stable organic-mineral bonds through anion and inner-sphere ligand-exchange reactions. Crystallisation and dehydration processes transform ferrihydrite into the strongly crystalline minerals goethite (α-FeOOH) and haematite (α-Fe_2O_3) which have a lower surface area and charge density and consequently a lower affinity for SOC (Torn et al. 1997). The amount of oxides and their crystallinity has been identified as a controlling factor for SOC concentrations and turnover (Torn et al. 1997). For example, OM mineralization in coniferous forest soils was found to be significantly reduced in the presence of short range order minerals such as ferrihydrite and Al silicates such as allophane (Rasmussen et al. 2008).

Fe and Al oxides are often studied together because Fe oxides such as goethite and haematite undergo isomorphic substitution of Fe with Al, but in contrast with Al, the stability of Fe oxides is affected by the redox status of the soil. In general, there is a depth-related transition from oxidising conditions in the upper sections to reducing conditions in the underlying sections of a soil. Gley soils, however, are characterised by highly localised patterns of Fe oxides depletion and enrichment related to the reduction of ferric (Fe^{3+}) and mobilisation of ferrous (Fe^{2+}) ions in anaerobic regions and the reoxidation and subsequent precipitation as Fe^{3+} oxides in oxidising areas of the soil. These redox processes give gley soils characteristic brown mottles which are indicative of localised re-oxidation of

Fe. Importantly, precipitates rich in both Fe and OM can also form, especially if interchanging redox conditions prevail (Kalbitz and Kaiser 2008). As a consequence of the temporal and micro-spatial variability in redox conditions, the stabilisation of SOM via interaction with Fe/Al oxides and therefore the C turnover in gley soils is a highly complex process. The role of Fe and Al oxides in SOC dynamics and especially the nature of the interactions between SOC and Fe/Al oxides in these gley soil systems is not well-defined. The specific aims of this pedological and geochemical study are to:

i) determine changes in total SOC and N contents, proportions of Fe/Al oxides and SOC and N contents associated with Fe/Al oxides within the profiles of gley (Stagnosol and Gleysol) soils under contrasting hydrological regimes and freely draining control (gleyic Cambisol) soils.

ii) characterise Fe/Al oxide crystallinity within the soil profiles using sequential selective dissolution and explore whether Fe/Al oxide crystallinity increases in gleyed soils experiencing more redox oscillations than freely draining soils.

iii) investigate chemical characteristics of OM associated with Fe/Al oxides within the soils.

The following questions will be addressed:

i) Do soil properties (e.g. SOC, N, total Al and Fe contents), proportions of Fe/Al oxides (total, weakly and strongly crystalline) and SOC and N contents associated with Fe/Al oxides differ significantly between gley soils?

ii) Do soil C/N ratios differ significantly in Stagnosols, Gleysols and gleyic Cambisols before and after removal of SOC and N associated with Fe/Al oxides?

iii) Are whole and extractable SOC contents in Stagnosols, Gleysols and gleyic Cambisols linearly correlated with Fe/Al oxide phases (total, weakly and strongly crystalline)?

2. Materials and methods

2.1. Site and sampling

The study site was Harwood Forest, Northumberland, UK (BNG NY 995 944), a commercially managed Sitka Spruce (*Picea sitchensis* (Bong.) Carr.) plantation. This site has been the subject of previous soil carbon and greenhouse gas investigations (Zerva et al. 2005; Ball et al. 2007;

Mojeremane et al., 2010). Mean annual rainfall is approximately 950 mm and mean air temperature is 7.6 °C. The forest covers an area of gentle slopes (< 10^{o}) at altitudes of between 200 and 400 m above ordnance datum. Soils studied here are described by Wilson et al. 2013. The underlying parent material is dominated by till and drift deposits derived from Paleozoic sandstones, mudstones and shales; these support Histosols, Gleysols, Stagnosols, Podzols and small areas of Cambisols (Avery, 1973; FAO, 2006). The chosen soils were histic Gleysol, histic Stagnosol, and gleyic Cambisol (FAO, 2006). Inceptisols, Aquepts, Endoaquepts, Humic Endoaquepts (Order, Suborder, Great Group, Subgroup) was the dominant soil type according to the US soil classification system (Soil Survey Staff, 2010). The Gleysol profiles formed in sedimentary deposits on the margins of Fallowlees Loch, a small groundwater basin lake, were affected seasonally by rises and falls in the groundwater levels. By contrast, the Stagnosol profiles were situated on a gentle (5-10 ^{o}) slope and drainage in the upper part of the profile was restricted by the clay loam subsoils derived from the local glacial drift geology. The Cambisol was located on an area of coarser textured sedimentary deposits alongside a small stream and although the deeper subsoil exhibited some evidence of gleying, the upper 45 cm was relatively free-draining (see Table 1 and Wilson et al. 2013 for further details). Soils were taken from grassy clearances within the forest in spring 2009. Five replicate soil pits at randomly selected locations, placed at least 5 m apart, were opened at each of the gley soil (Stagnosol and Gleysol) sites and one soil pit was opened at the control (Cambisol) site. Mineral topsoil (10-20 cm depth) and subsoil (20-30 cm depth) samples of known volume were collected using a monolith tin (50 cm l x 15 cm b x 7 cm d). Three replicate intact soil samples were taken at each soil depth for each of the pits and bagged separately. For selected sites, single (not replicate) organic topsoil samples were taken at 0-10 cm (surface vegetation not included). Soils were transported to the laboratory, weighed, air-dried as intact soil sections, reweighed and passed through a 2-mm sieve.

2.2. Physical analyses

Bulk density, water content and percent water-filled pore space (WFPS) were determined for soil samples (Robertson et al., 1999). Soil sub-samples were dried at 105 °C over 16 hours to correct values for oven-dried moisture contents and where necessary, weights and estimated volumes of large stones removed during sieving were recorded to calculate corrected bulk density values. WFPS was then estimated for mineral soils according to Robertson et al. (1999) using a standard particle density value

of 2.65 g cm^{-3}. For organic topsoils it was expected that particle densities would be considerably lower than 2.65 g cm^{-3} and therefore WFPS was not calculated.

2.3. Sequential extractions

Acid ammonium oxalate extracts weakly crystalline Al^{3+} and Fe^{3+} oxides and SOM bound to these phases but it does not solubilise crystalline oxides (von Lützow et al. 2007). Extraction with dithionite-citrate-bicarbonate (DCB) disrupts Al^{3+} and Fe^{3+} bonds between minerals and SOM by reductive dissolution and concurrently releases SOM from both weakly and strongly crystalline Al^{3+} and Fe^{3+} oxides into solution (von Lützow et al. 2007). If the weakly crystalline oxides have first been removed, DCB can, however, be used as a selective extractant for strongly crystalline oxides. In this study, weakly and then strongly crystalline Fe/Al oxides, along with the respective associated OM fractions, were extracted from soil sub-samples for each replicate at each depth within each soil pit, by sequential selective extraction using oxalate and then DCB. To isolate oxalate-soluble Al, Fe and bound OM, 0.02 M ammonium oxalate (pH 3) (Schwertmann 1964; van Oorschot & Dekkers 2001) was used in preference to 0.2 M ammonium oxalate to minimise oxalate contamination of extracted OM and remaining soil residues. To compare the efficiency of the 0.02 M and 0.2 M ammonium oxalate extraction methods, test extractions using the conventional 0.2 M ammonium oxalate method were carried out for selected single soil sub-samples from 10-20 cm and 20-30 cm depths for each pit (see Supplementary Digital Content Table 1 for further details). Isolation of DCB-soluble Al, Fe and bound OM from the oxalate-extracted soil residues was performed using the DCB method (Mehra & Jackson 1960; van Oorschot & Dekkers 1999). Extracted soil residues were then rinsed twice with deionised water to remove contaminants and dried (30 °C; 48 hours) prior to total C and N analysis and total digestion (see Section 2.4).

2.4. Chemical analyses

Soil pH values for sub-samples of each replicate were determined in soil solutions (air-dried soil:deionised water ratio 1:2) using a Spectronic Model 3505 pH meter (Spectronic, Leeds, UK). OM contents (calculated by loss on ignition at 450 °C for 16 hours) and total C and N concentrations were determined (Carlo-Erba NA 1500 Elemental Analyser (Carlo-Erba, Milan, Italy)) for whole soils and extracted soil residues (correcting for oven-dried % moisture). Total soil C was assumed to be equal to

total OC as the parent material is not calcareous (Zerva et al. 2005). The amount of OC and N associated with Fe/Al oxides was determined by subtracting OC and N contents in the extracted soil residues from those in the whole soils. Soil texture was measured for selected soil samples using a laser diffraction Coulter counter (Coulter LS230). Representative soil samples < 2000 µm were pre-treated to remove organic materials using 15% H_2O_2 and 0.1% $Na_6P_6O_{18}$ was added as a dispersant (Wilson et al. 2009).

The Al and Fe concentrations in the oxalate and DCB extract solutions, and total Al and Fe concentrations in whole soils and extracted soil residues (after microwave-assisted HNO_3/HBF_4 or HNO_3/HF digestion using a modified US EPA 3052 method) were determined using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), equipped with a gem-cone cross-flow nebuliser and AS 93 plus autosampler. Typical internal analytical precision (±1 SD) for Al and Fe determination in extract and digest solutions was $\leq \pm$ 5%. Calculated total and extractable soil Al and Fe concentrations were corrected for oven-dried % moisture. Accuracy of total concentration data was confirmed by quality control analyses of three certified reference materials alongside samples; silty clay loam soil (CRM No. 7003), ombrotrophic peat (NIMT/UOE/FM001) and coal (NBS SRM 1635). Determined concentrations on average were 85-95 % (Fe) and 92-95 % (Al) of the certified values.

2.5. Control extractions

Control extractions using 0.049 M sodium sulfate (Na_2SO_4) were performed according to Wagai & Mayer (2007) to account for levels of labile SOC (Kaiser et al. 2011) and Fe and Al that are soluble in water and ion-exchangeable by oxysulfur anions, such as oxidation products of dithionite (Wagai & Mayer 2007). These control extractions allowed differentiation between released particulate OC and released OC associated with Fe/Al oxides. Selected single Harwood forest soil sub-samples from 0-10 cm, 10-20 cm and 20-30 cm depths for each pit were extracted. Extractable dissolved OC concentrations were determined using a Shimadzu 6000 TOC (High Temperature Catalytic Oxidation) analyser and extractable Fe and Al concentrations were determined using ICP-OES.

Test extractions using a 0.3 M solution of the organic-C based complexing agent sodium citrate ($Na_3C_6H_5O_7$), as used in the DCB extraction method, were also performed for the selected sub-samples. Sodium citrate extracts Fe/Al oxide-associated OM as well as some OM associated with other mineral components (e.g. Al silicates). Also, like sodium sulfate, sodium citrate may extract labile forms of OM. The purpose of these extractions therefore was to compare levels of SOC extracted by sodium citrate with those extracted by the sodium sulfate control. Dissolved OC concentrations were determined in sodium citrate extracts after blank subtraction to evaluate the proportion of SOC associated with Fe/Al oxides and other mineral components and any extractable labile SOC.

2.6. Purification of extracted OM and analysis using FT-IR spectroscopy

Selected extract solutions were dialysed (dialysis tubing, MW cut-off 7000 Daltons, Medicell International Ltd. dialysis membrane) against deionised water and water was changed every 24 hours until the pH inside the dialysis tubing was approximately 6.5. Purification of extracts was necessary to remove oxalate and citrate contaminants. Noisy FT-IR spectra obtained for undialysed oxalate and DCB extracts, particularly in comparison to dialysed oxalate and DCB extracts, confirmed this (data not shown). Blank oxalate and DCB extract solutions were also dialysed to check that purified extracts changed from cloudy to clear. The purified extracted OM samples were freeze-dried and FT-IR spectra were acquired in transmission mode with a Jasco FT/IT-460 Plus FT-IR spectrometer. Approximately 0.5-1 mg freeze-dried OM was mixed with KBr in a ratio of ~ 1:100. Background corrected spectra were obtained in the range of 3600-500 cm^{-1}, with 2 cm^{-1} resolution and 64 scans per sample. The absorption bands were assigned according to Stevenson (1994). For comparison with extracted OM, FT-IR spectra for Gleysol 10-20 cm and 20-30 cm whole soils were recorded on a Bruker Vertex 70 FT-IR spectrometer using a Diamond Attenuated Total Reflectance accessory.

2.7. Statistical data analyses

Measurement values for replicate sub-samples from each pit (experimental unit) were averaged or, in the case of Gleysol and Stagnosol 0-10 cm soils, single samples from pits were averaged, and those means were statistically analysed using MINITAB version 15. The significance of differences in soil measurements at each soil depth for Gleysols and Stagnosols were tested using independent t-tests (summary of results presented in Table 5). Data were checked for normality before t-tests were applied.

Differences between soil types were deemed significant if $P \leq 0.05$. Data for the Cambisols could not be included in statistical data analyses because only one soil pit (i.e. one experimental unit) was sampled. Paired t-tests were also used to compare data obtained for soil samples extracted using two different oxalate concentrations (Supplementary Digital Content Table 1) and whole soil C/N ratios with those of extracted soil residue C/N ratios in matched samples. Linear relationships between measured SOC/extractable SOC contents and amounts of different extractable Fe/Al oxides ($Fe_{DCB,}$ $Al_{DCB,}$ $Fe_{O,}$ Al_{O}, Fe_{DCB-O} and $(Fe + Al)_{O}$) were assessed using simple linear regression analysis (Supplementary Digital Content Figs. 1 and 2).

3. Results

3.1 Physical and chemical soil properties

Visual observations confirmed that the three soil types exhibited different profiles and the gley (Gleysol and Stagnosol) soils consisted of humified organic rich Ao surface layers approximately 10 cm deep overlying mottled mineral soils with A horizons approximately 10 cm deep. Soil profile descriptions and physical and chemical characteristics of Harwood forest soils are summarised in Table 1. In the Gleysol, which is influenced by groundwater fluctuation, the surface organic horizon grades into an organo-mineral A horizon. In the Stagnosol, which is dominated by a perched water table, the distinction between the organic and mineral horizons is sharper with the organic horizon giving way to a gley organo-mineral A horizon. All three profiles exhibited evidence of gleyic processes in the form of Fe masses and nodules, but these were found to be more frequent and more distinct in the gley soils than in the Cambisol. In the Stagnosol, Fe mottling occurred at a shallower depth (ca. 15 cm) than in either the Gleysol or Cambisol, reflecting the presence of restricted drainage in the upper soil horizons (Wilson et al., 2013).

Soil water contents were consistent with typical values previously measured for Harwood forest soils in Spring (Ball *et al*., 2007). Water and OM contents dropped markedly on going from the 0-10 cm (Ao horizon) to the 10-20 cm (A horizon) with depth for all three soils but, as expected, Gleysol and Stagnosol 0-10 cm soils had much higher water (~80-100 %) and OM (~24 %) contents than the freely draining Cambisol control soils (water content ~50-70 % and OM contents ~5-9 %). WFPS values

(~50-80 %) were similar for all three mineral soils, being highest in the 10-20 cm mineral soils. Bulk densities increased with depth from ~0.5 to ~1.0 g cm^{-3} due to increasing soil compaction and mineral contents. All soils were acidic, albeit the Cambisol soils were slightly less acidic (pH ~5.1-5.4) than the gley soils (pH ~3.9-4.7), and pH values remained fairly constant with depth (Table 1). Soil textures were similar (sandy loam) for the 0-10 cm and 10-20 cm soils of all three soil types but clay contents in the poorly draining Gleysol and Stagnosol 20-30 cm soils were higher (silt loam) than those for the Cambisol (loamy sand) (Table 1).

3.2. Soil C and N

Concentrations of soil OC and N in Gleysols, Stagnosols and Cambisols are shown in Table 2. Soil OC and N stocks were calculated for complete soil profiles from which 0-10, 10-20 and 20-30 cm soil sections were collected. Total soil OC and N stocks from 0-30 cm in the Gleysol (5 pits) (92 ± 29 and 4.5 ± 1.3 t ha^{-1}, respectively) and Stagnosol (2 pits from which 0-10, 10-20 and 20-30 cm sections were collected) (90 ± 20 and 4.8 ± 1.5 t ha^{-1}, respectively) soils were similar and soil OC and N stocks decreased with depth (Fig. 1). Calculated total OC and N stocks from 0-30 cm for the Cambisol (1 pit) (51 and 3.4 t ha^{-1}, respectively) soils were lower than those calculated for the gley soils due to the much lower contribution to total OC and N stocks from the 0-10 cm Cambisol organic topsoil layer (Fig. 1). Soil OC and N stocks at different depths for the Gleysols and Stagnosols were not significantly different ($P > 0.05$, Table 5). Overall, calculated stocks are consistent with those measured for similar soils collected from Harwood forest (Zerva et al. 2005; Ball et al. 2007). In all soils, soil OC and N concentrations were lowest (~1.5-1.9 % and ~0.08-0.09 %, respectively) in the 20-30 cm soils. Gleysol and Stagnosol OC and N concentrations decreased strongly with depth throughout the profile, whereas for the Cambisol, highest values were found in the 10-20 cm mineral topsoil layer (Table 2). Soil C/N ratios were highest in the Gleysols, suggesting that they were less humified than the Stagnosols and Cambisols. With increasing depth, Gleysol and Stagnosol C/N ratios remained approximately constant (~20-21 and ~18-19, respectively) but Cambisol C/N ratios varied (range ~13-20).

3.3. Soil Al and Fe

Total Al and Fe concentrations (mg g^{-1}) in Gleysols, Stagnosols and Cambisols are shown in Table 3. Total Al and Fe concentrations increased with depth and were highest in the Gleysol 10-20 and 20-30

cm mineral soils. Stagnosol and Cambisol total Fe concentrations remained fairly constant with increasing depth while total Al concentrations decreased (Table 3). Total Fe concentrations in the 20-30 cm Gleysols were significantly higher (P = 0.001) than those found in the corresponding 20-30 cm Stagnosols (Tables 3 and 5), suggesting that contrasting gley soil hydrological regimes had an effect on total subsoil concentrations of the redox-sensitive element, Fe.

3.4. Soil extractable elemental concentrations

Test extractions using the conventional 0.2 M oxalate method (see Section 2.3) indicated that the Al and Fe extraction by the 0.02 M oxalate method averaged 48 ± 19 % and 23 ± 9 %, respectively, of those extracted by the conventional method (see Supplementary Digital Content Table 1). For this reason, 0.2 M oxalate extraction Fe and Al values, rather than 0.02 M oxalate extraction values, were used to calculate the amounts of weakly and strongly crystalline Fe and Al oxides present in these soils (Table 4 and Supplementary Digital Content Table 1).

For clarity and to be consistent with terminology used in cited studies, the following abbreviations will be used in this paper: Fe_O and Al_O correspond to oxalate extractable Fe and Al concentrations, respectively, and represent the amounts of weakly crystalline Fe/Al oxides. Since sequential extractions were carried out in this study using 0.02M oxalate followed by DCB extractions, DCB extractable Fe (Fe_{DCB}) and Al (Al_{DCB}) correspond to total extractable Fe and Al concentrations (i.e. the sum of sequential 0.02 M oxalate and DCB extractable Fe and Al concentrations) which represent the total amounts of weakly and strongly crystalline Fe/Al oxides. Fe_{DCB-O} and Al_{DCB-O} correspond to Fe_{DCB} - Fe_O and Al_{DCB} - Al_O, respectively, where Fe_O and Al_O are conventional 0.2 M oxalate extractable Fe and Al concentrations (i.e. total Fe/Al oxide concentrations subtracting weakly crystalline Fe/Al oxide concentrations). Thus, Fe_{DCB-O} and Al_{DCB-O} are measures of strongly crystalline Fe and Al oxides.

3.4.1. Control extractable Fe, Al and C

Control (Na_2SO_4) extractable SOC and Fe concentrations were detectable in only some of the selected samples, whereas control extractable Al concentrations were detectable in most of them. As a proportion of total extractable concentrations of SOC, Fe (Fe_{DCB}) and Al (Al_{DCB}), control extractable concentrations of SOC, Fe and Al ranged from 0.6-3 %, 0.01-0.14 % and 0.08-13 %, respectively. For Al, proportions greater than 10 % were only found in a fifth of the control samples. Therefore, control

extractable concentrations of SOC, Fe and Al concentrations were considered to be negligible or minor. Control extractable concentrations were not subtracted from corresponding oxalate and DCB-extractable SOC, Fe_{DCB} and Al_{DCB} concentrations, which were assumed to represent total Fe/Al oxide associated concentrations. As a proportion of total extractable SOC, sodium citrate extractable SOC ranged from 7-38 %. Sodium citrate extracted up to approximately 15 times more SOC than the sodium sulfate controls confirming that the majority of the SOC extracted using the DCB procedure was associated with Fe/Al oxides, although contributions from other mineral components were possible.

3.4.2. Total Fe and Al oxide contents

Fe_{DCB} and Al_{DCB} concentrations were calculated as the sum of sequential 0.02 M oxalate and DCB extractable Al and Fe concentrations. Table 3 summarises Al_{DCB} and Fe_{DCB} concentrations for the Gleysols, Stagnosols and Cambisols. Greatest concentrations of Fe_{DCB} and Al_{DCB} occurred in the Gleysol 10-20 cm and 20-30 cm mineral soils and values were approximately two to three times greater than those in the corresponding organic 0-10 cm Gleysols (Table 3). By contrast, Stagnosol and Cambisol Al_{DCB} and Fe_{DCB} concentrations remained fairly constant or showed more gradual increases with depth. Al_{DCB} constituted around a tenth of Fe_{DCB} in all three soils, the only exception being Al_{DCB} in the 0-10 cm Gleysol, which constituted a fifth of Fe_{DCB} concentrations (Table 3). Fe_{DCB} concentrations in the 10-20 cm and 20-30 cm Stagnosols were not significantly different from each other ($P > 0.05$) and were not significantly different ($P > 0.05$) from those in the corresponding Gleysols (Table 5). Al_{DCB} concentrations in the 10-20 cm and 20-30 cm Stagnosols, however, were found to be significantly less ($P = 0.021$ and 0.032, respectively) than those in the corresponding Gleysols (Table 5).

3.4.3. Weakly crystalline Fe and Al oxide contents

Table 3 summarises Al_O and Fe_O for the Gleysols, Stagnosols and Cambisols. Based on extraction data for selected soils, comparison of 0.02 M and 0.2 M oxalate-extractable concentrations of Al and Fe for Gleysols, Stagnosols and Cambisols (Supplementary Digital Content Table 1), 0.02 M and 0.2 M oxalate extractable Al and Fe concentrations generally exhibited the same trends for all three soil types. Fe_O decreased with depth and, with the exception of the Stagnosol soils, Al_O increased with depth (Table 3 and Supplementary Digital Content Table 1). Fe_O concentrations in the 10-20 cm and 20-30

cm Stagnosol soils were not significantly different ($P > 0.05$) than those in the corresponding Gleysols. Al_O concentrations in the 20-30 cm Stagnosol soils, however, were significantly lower than those in the corresponding Gleysols ($P = 0.022$) (Table 5), suggesting that less saturated gley soils had lower weakly crystalline Al oxide concentrations than more saturated soils at the same depths.

3.4.4. Strongly crystalline Fe and Al oxide contents

Fe_{DCB-O} contents were calculated using 0.2 M oxalate extractable Fe concentrations determined for selected 10-20 and 20-30 cm soil sections (Table 4 and Supplementary Digital Content Table 1). With the exception of the 10-20 cm Stagnosols, the majority of the total Fe oxides present in these soils occurred as strongly crystalline phases. By contrast, the majority of the total Al oxides present occurred as weakly crystalline phases. Note that Al_{DCB-O} contents are not shown in Table 4 as in some cases Al_O (0.2 M oxalate method) concentrations were equal to or greater than concentrations of Al_{DCB}. Fe_{DCB-O} concentrations were significantly lower in the 10-20 cm than the 20-30 cm Stagnosols ($P = 0.024$) but not in the corresponding Gleysols ($P > 0.05$, Table 5). This suggests that differences in hydrological and redox conditions within the Stagnosol profile influenced strongly crystalline Fe oxide concentrations with higher levels occurring in the more oxidised 20-30 cm soil layer (see Section 4.1).

3.5. Fe/Al oxide associated C and N

Calculated 0.02 M oxalate and DCB extractable SOC and N concentrations (i.e. amounts of C and N associated with Fe/Al oxides) for Gleysols, Stagnosols and Cambisols are shown in Table 2. As for total SOC and N concentrations, extractable OC and N concentrations decreased with depth in the Gleysols and Stagnosols. In general, for Gleysols at all depths and 10-20 cm and 20-30 cm in the Stagnosols and Cambisol, 70-90 % of the SOC and soil N were associated with Fe/Al oxides with much lower levels of soil OC and N being found in the 0-10 cm Stagnosol (48 %) and Cambisol (22 %) soils (Table 2). Calculated soil OC and N concentrations associated with Fe/Al oxides for Gleysol and Stagnosol profiles were not significantly different ($P > 0.05$) (Table 5) even though significantly different amounts of Fe/Al oxides within these soils were found. This could be due to contributions from SOC associated with other extractable mineral components during the selective dissolution procedures.

3.6. Extracted soil residue C and N contents

Concentrations of SOC and total N in extracted soil residues for Gleysols, Stagnosols and Cambisols are shown in Table 2. In all three soil types, soil residue OC and total N concentrations decrease with increasing depth which, with the exception of the low whole soil OC and total N concentrations observed for the 0-10 cm Cambisol, is consistent with trends observed for corresponding whole soil OC and total N concentrations. Soil residue OC and total N concentrations and C/N ratios determined for Gleysol and Stagnosol profiles were not significantly different ($P > 0.05$). For all three 10-20 cm and 20-30 cm soils, measured residue C/N ratios were significantly lower (paired t-test, $P < 0.05$) than the corresponding whole soil C/N ratios (Table 2). In contrast, 0-10 cm Gleysol and Stagnosol soil residue C/N ratios were higher (but not significantly, paired t-test, $P > 0.05$) than those found for the whole soils (Table 2).

3.7. Chemical characteristics of SOM associated with Fe/Al oxides

Selected FT-IR spectra obtained for sequential oxalate and DCB extractable OM, for 10-20 cm and 20-30 cm Gleysols, Stagnosols and Cambisols, are shown in Figures 2 and 3, respectively. Extracted OM exhibited the typical absorption bands of humic substances in the following regions: 3400 cm^{-1} (H-bonded OH groups), 2900 cm^{-1} (aliphatic C-H stretching), 1600-1560 cm^{-1} (C=O of amide groups, quinone and/or ketones, aromatic C=C, COO^- symmetric stretching, N-H deformation and C=N stretching) 1370 cm^{-1} (OH deformation and C-O stretching of phenolic OH, COO^- antisymmetric stretching, C-H deformation of CH_2 and CH_3 groups) and 1000 cm^{-1} (C-O stretching of polysaccharide or polysaccharide-like substances and/or Si-O stretches of silicates if present in extracts). In general, absorption bands for DCB extractable OM were broader at 3400 cm^{-1}, stronger at 2900 and 1370 cm^{-1} and weaker at 1000 cm^{-1} relative to those for oxalate extractable OM. In general, similar FT-IR spectra trends were observed for all three soil types and soils from different depths (Figs 2 and 3). Gleysol 10-20 cm and 20-30 cm whole soil FTIR spectra (Fig. 4) confirm that the oxalate and DCB extraction procedures extracted the expected important organic moieties.

4. Discussion

4.1 Proportions of Fe/Al oxides in gley soil profiles

For the soils studied here, it was found that total extractable Al and Fe oxides comprised 5-11 % and 40-90 % of the total soil Al and Fe, respectively (Table 3), indicating that Fe oxides are more dominant than Al oxides in these soils. Similarly Bascomb (1968) found that considerable amounts of Fe oxides, particularly well-crystallised Fe oxides, were present in a range of gley and well-drained brown earth soil profiles from the UK. Also, Gasparatos et al. (2004) found that 78 % of the total Fe content in concretions from imperfectly drained Greek alfisol soils existed in the form of Fe oxides. In the Gleysols and Stagnosols studied here, highest Fe oxide contents were found in the zones of maximum gleying, i.e. at depths of 10-20 and 20-30 cm (Tables 1 and 4), supporting findings from a similar study of gley soils from the Yorkshire Warplands (Bloomfield 1952). Strongly crystalline oxides comprised 50-80 % of the total soil Fe oxides in all the Harwood forest mineral soils (Table 4), confirming the dominance of strongly crystalline Fe oxides such as goethite in these temperate acid soils (Eusterhues et al., 2003).

Interestingly, the Stagnosol 10-20 cm soils had noticeably lower (not significantly lower, $P = 0.059$, see Table 5) amounts of total Fe oxides compared with corresponding Gleysols. Differences could not be tested statistically but Stagnosol 10-20 cm total Fe oxide concentrations were also noticeably lower than those in the Cambisol 10-20 cm soils. Only approximately one fifth of the total Fe oxides present in these 10-20 cm Stagnosol soils comprised strongly crystalline Fe oxides. These trends could be explained by contrasting hydrological regimes and soil redox conditions in Gleysol and Stagnosol profiles. As supported by colour and mottling observations (Table 1), it is likely that the Stagnosol 10-20 cm soils were more strongly reduced and the 20-30 cm soils were more strongly oxidised than the corresponding Gleysol horizons. The significantly lower Al_{DCB} concentrations in the 10-20 cm and 20-30 cm Stagnosol soils compared with those in the corresponding Gleysols (Section 3.4.2) is surprising because Al oxides are less likely to be influenced by contrasting gley soil redox processes than Fe oxides. Also, pH values for both Gleysols and Stagnosols were very similar so changes in soil pH cannot explain these differences. This finding could be attributable to Al substitution within the Fe oxides in the Gleysols and Gleysol sesquioxides having less dominance of Fe than Stagnosol sesquioxides.

Thompson et al. (2006) directly demonstrated that Fe oxide crystallinity increased during soil redox oscillations. Redox reactors were used to study soils subjected to a series of reduction-oxidation cycles

and the cumulative response of soil solids during multiple redox oscillations included a decrease in concentrations of oxalate extractable Al and Fe and a transformation of short range order Fe (present in the studied soils as nano-goethite) to micro-crystalline goethite and micro-crystalline haematite (Thompson et al. 2006). For the Harwood Forest soils studied here, with the exception of the Stagnosol 10-20 cm soils, concentrations of strongly crystalline Fe oxides were indeed higher (and therefore oxalate extractable Fe concentrations were lower) in the redox-dynamic gley soils than the freely draining Cambisol soils (Tables 3 and 4) but this was not the case for Al oxides. Field (Table 1) and micromorphological (Wilson et al., 2013) evidence support the taxonomic classifications of Gleysol and Stagnosol but statistically significant differences between the Gleysol and Stagnosol with regard to SOC storage and Fe oxide crystallinity were generally not found. Micromorphological examination of these gley soils, teamed with Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry, suggested that hydrological differences were not great enough to differentially affect the development of redoximorphic conditions and therefore levels of Fe oxide crystallinity (Wilson et al., 2013).

4.2 Calculated Fe_O/Fe_{DCB} ratios for gley soils

The active Fe ratio (Fe_O/Fe_{DCB}) is a measure of the proportion of weakly crystalline Fe oxides within total Fe oxides, providing a useful indication of the degree of crystallinity of Fe oxides in soils in general. It is useful because it reflects the different environmental conditions (e.g. redox) under which Fe oxides have been precipitated and transformed (Mansfeldt et al. 2012). Soils with a low proportion of weakly crystalline Fe components typically have Fe_O/Fe_{DCB} ratios <0.2 and $(Fe + Al)_O$ <10 mg g^{-1} (Mikutta et al. 2006). As the 0.02 M oxalate extraction method was found to be less efficient than the conventional 0.2 M oxalate extraction method, Fe_O/Fe_{DCB} ratios and mean $(Fe + Al)_O$ concentrations were calculated for samples extracted using 0.2 M oxalate (Table 4 and Supplementary Digital Content Table 1). Calculated Fe_O/Fe_{DCB} ratios for all soils at depths of 10-20 and 20-30 cm suggest that, with the exception of the 10-20 cm Gleysols which had ratios <0.2 and were found to be significantly lower than those in the corresponding Stagnosols ($P = 0.001$, Table 5), these soils generally contained high proportions of weakly crystalline Fe components. Mean $(Fe + Al)_O$ concentrations for the soils at depths of 10-20 and 20-30 cm were all below 10 mg g^{-1} (Table 4) and there were no significant differences between Gleysol and Stagnosol mineral soils ($P > 0.05$, Table 5), but these low values are

likely to be attributable to the low concentrations of weakly crystalline Al (Al_O) relative to those of Fe (Fe_O) found in these Harwood forest soils.

4.3 OM accumulation and proportions of OM associated with Fe/Al oxides in gley soil profiles

Several mechanisms may be responsible for the chemical interactions between OM and Fe/Al oxides in gley soils. The chemical nature of the organic material (e.g. functional group content, hydrophobicity, molecular size), the type of mineral (e.g. goethite, hematite) and specific surface area of mineral particles are key factors (Krull et al. 2003). The Gleysols, Stagnosols and Cambisols studied here were acidic ($pH \leq 5$) (Table 1) and are therefore expected to be rich in Fe and Al oxide surfaces with protonated hydroxyl groups which are important for C stabilisation (Eusterhues et al. 2005a; Kiem and Kögel-Knabner 2002). Interactions between these Fe/Al oxide surfaces and OM can be strong (e.g. inner-sphere ligand exchange interactions between OH groups on Fe and Al oxides surfaces and OM with carboxyl and phenolic OH groups) and/or weak (e.g. electrostatic interactions such as van der Waals forces between protonated/positively charged functional groups on both Fe/Al oxides and OM surfaces at low pH or outer-sphere interactions) (von Lützow et al. 2006). Soil OC and N stocks generally decreased with depth (Fig. 1), consistent with typical trends of decreasing SOM contents with depth but greater fractions of total SOM are likely stabilised by minerals in subsurface horizons due to intimate associations of humified OM with minerals at these depths (Kaiser et al. 2002). A recent ^{14}C study estimated total soil C mean residence times of between 181 and 305 years for organic topsoils and 1072 and 1381 years for mineral subsoils from Harwood Forest (Burns 2011), suggesting that mineral stabilisation mechanisms are important in Harwood Forest subsoils.

Oxalate and DCB-extractable SOC concentrations were broadly similar for all three of the 10-20 cm (1.7–2.8 %) and 20-30 cm (1.3–1.5 %) soils and compared with the organic 0-10 cm soils, higher levels of soil OC and N were associated with Fe/Al oxides (Table 2). These findings further confirm the importance of organo-Fe/Al oxide associations (Wilson et al. 2013; Falsone et al. 2013) and strong correlations between the presence of SOM and the presence of Fe pedofeatures in mineral soils from all three soil types. The lower levels of OC and N associated with Fe/Al oxides in the organic topsoils is likely to be attributable to the OM in these soils being fresher and less decomposed/humified than OM in underlying mineral soils (as indicated by C/N ratio trends in Table 2), and therefore containing fewer reactive functional groups (e.g. COOH groups (see Section 4.4))

with which to interact with soil minerals (Kaiser et al. 2011). Also, Rasse et al. (2005) suggested that the interaction of root-derived organic acids with mineral surfaces in subsurface soils with low OM contents may be more effective than in OM-rich surface soils because subsurface soil mineral surfaces are not yet saturated with OM. Therefore, another explanation for the low proportions of total OM associated with Fe and Al oxides in the Harwood Forest 0-10 cm organic topsoils could be the high loadings of OM and insufficient amounts of reactive Fe/Al oxide surfaces for the OM to interact (Tables 1 - 3). Overall, for these Harwood Forest soils, whole SOC contents appear to vary independently of Fe and Al oxide contents (Tables 2 and 3) which could be attributable to variable surface loadings, depending on different organic inputs with depth, as found by Kaiser et al. (2002) for two contrasting acidic forest soil profiles.

Enrichment and depletion patterns of OM associated with Fe/Al oxides in gley soils are controlled by hydrological regimes (low mineralisation activity due to water saturation and decreasing oxygen availability being an important mechanism for OM enrichment) and redox-facilitated transport processes (see Section 1). Although speculative, the transport of dissolved OM and Fe/Al through lateral subsurface water movement may also have occurred in the Stagnosol soils as they were situated on a gentle (5-10°) slope (see Section 2.1 and Wilson et al. 2013). However, as mentioned in Section 4.1, the absence of significant differences between SOC storage in the Gleysols and Stagnosols studied here (Section 3.2) may be due to hydrological differences not being great enough to differentially affect the development of redoximorphic conditions and therefore contrasting OM enrichment and depletion patterns in the whole gley soils studied here were not detected. Falsone et al. (2013) conducted a micromorphological study of the SOM in the gley mineral soils considered here and found that the transformation of SOM and/or the formation of organic-inorganic associations were important C stabilisation mechanisms. Indeed small water retention pores were found to be associated with Fe-rich amorphous organic features, indicating that soil porosity coupled with water stagnation affected Fe-SOM interactions and the accumulation of transformed organic compounds in these gleyed soils (Falsone et al. 2013).

4.4 Preferential affinity of organic compounds for Fe/Al oxides

Stagnosol, Gleysol and gleyic Cambisol 10-20 cm and 20-30 cm mineral soil C/N ratios were found to be significantly different before and after removal of SOC and N associated with Fe/Al oxides. Oxalate

and DCB extracted soil residue C/N ratios (i.e. after removal of SOC and N associated with Fe/Al oxides) determined for Stagnosol, Gleysol and gleyic Cambisol mineral soils, were significantly lower than corresponding whole soil C/N ratios (Section 3.6). This could indicate that more labile, less decomposed OM was preferentially extracted by the oxalate and DCB methods, implying that this type of OM is associated with Fe/Al oxides in mineral soils but it is worth noting that some OM not associated with Fe/Al oxides is likely to have also been extracted (see Section 3.4.1). The lack of similar significant differences for topsoil (0-10 cm) C/N ratios (Section 3.6) is most likely due to high OM loadings of fresh OM and insufficient amounts of reactive Fe/Al oxide surfaces for the OM to interact (see Section 4.3). Sorption of OM to mineral surfaces is not homogeneous and fractionation of organic compounds occurs during the sorption process (Kaiser and Zech 2000). Spielvogel et al. (2008) reported that a specific fraction of the OC pool consisting of O/N-alkyl C and microbially-derived carbohydrates is preferentially stabilised by association with Fe and Al minerals in acid subsoils. Another explanation for the trends observed for whole and residue subsoil C/N ratios could be that mineral phases unextractable by oxalate and DCB (e.g. minerals other than oxides and Al silicates) preferentially adsorb N-rich microbially processed compounds. It has been suggested that positively charged amino groups account for sorption of N-containing substances to minerals (Hedges and Oades 1997). Under the acidic Harwood Forest soil conditions, amino groups and Fe/Al oxides are likely to be predominantly positively charged and capable of forming strong inner-sphere interactions and/or weak interactions with each other, but positively charged amino groups may be particularly attracted to negatively charged clay minerals such as illite (Kaiser and Zech 2000). Preferential adsorption of N-rich OM on mineral surfaces and therefore low C/N ratios was observed by Wagai et al. (2009) for heavy mineral-dominant SOM fractions isolated via density fractionation. It is also worth noting, however, that the unextractable N-rich OM was likely to contain occluded particulate OM released after chemical destruction of aggregates.

The OM associated with weakly and strongly crystalline Fe/Al oxides in the Harwood soils studied here had high hydroxyl, aliphatic, carbonyl, aromatic, amide, phenolic, carboxylate and carbohydrate content (Figs 2 and 3). Differences in the chemical nature of the OM associated with weakly and strongly crystalline Fe/Al oxides were apparent and in general, the OM associated with strongly crystalline Fe/Al oxides has greater hydroxyl, aliphatic, carboxylate and phenolic character and less

carbohydrate character than OM associated with weakly crystalline Fe/Al oxides. These findings support those of previous studies. For example, it has been suggested that Fe oxides are strongly selective for hydrophobic aromatic compounds and high MW OM fractions (e.g. Kaiser & Guggenberger 2007) but hydrophilic OM, which contains more labile carbohydrates, adsorbs weakly to Fe oxide surfaces (Spielvogel et al. 2008). Also, Eusterhues et al. (2005a) found that C associated with Fe oxides is oxidation resistant aliphatic C.

4.5 Correlations between SOC contents and Fe/Al oxide phases

Correlation plots for the Harwood forest soils studied here indicated that SOC contents were not linearly related to amounts of total Fe and Al oxides, weakly crystalline Fe and Al oxides or strongly crystalline Fe oxides. Using values determined for each of the Harwood 10-20 cm and 20-30 cm soil profiles, no correlations ($R^2 < 0.03$) were found between total SOC contents and Fe_O (0.2 M), Al_O (0.2 M), Fe_{DCB-O} (0.2 M) and $(Fe + Al)_O$ (see Supplementary Digital Content Fig. 1). Also, no strong positive correlations ($R^2 < 0.04$) between either total or extractable SOC contents and amounts of Fe_{DCB} and Al_{DCB} for all soils at all depths (see Supplementary Digital Content Fig. 2). This is in contrast to other studies where close correlations between SOC contents and various measures of Al and Fe oxides in a range of soils have been found. For example, Oades (1988) demonstrated a positive relationship between SOC contents and the presence of substantial amounts of Al and Fe oxides. Kaiser & Guggenberger (2000) found strong positive correlations between SOC and dithionite-extractable (dithionite-only rather than DCB-extractable) Fe contents in topsoils and illuvial subsoils from 34 forest soils. Positive correlations between SOC content and non-crystalline Fe oxides in volcanic subsoils (Torn et al. 1997) and between SOC and oxalate extractable Fe and Al ($(Fe + Al)_O$) contents in French loamy soils across a range of depths (Rasse et al. 2006) have also been reported. Mikutta et al. (2006) even found that mineral-associated stable OC (isolated via density fractionation) related positively to the content of crystalline Fe oxides in soils with low amounts (Fe_O/ Fe_{DCB} ratios < 0.2) of more reactive weakly crystalline components.

Soil texture may be important since Kiem and Kogel-Knabner (2002) found positive linear correlations between OC and weakly and strongly crystalline Fe oxide contents for sandy soils but not loamy soils and it was suggested that, although stabilisation of OC via interactions of OM with Fe oxide surfaces was important for both sandy and loamy soils, this mechanism may be particularly

dominant in sandy soils. Interestingly, Kiem and Kogel-Knabner (2002) found that strongly crystalline Fe oxides made up 60 to 70 % of total Fe oxides in these loamy arable soils, consistent with findings for these sandy loam, silt loam and loamy sand Harwood soils (see Section 3.5) (Table 1). Indeed Eusterhues et al. (2005b) found positive correlations between organo-mineral associated C (OC_{min}), determined using density fractionation, and Fe_{DCB} and Fe_{O} concentrations in sandy, acid forest subsoils and it was suggested that topsoil organo-mineral associations did not follow the same trend as the underlying subsoils because they contained too much OC or insufficient amounts of Fe oxides for the OM to interact, as indicated by OC_{min}/Fe_{DCB} ratio values of ~ 1.5 and 1.4 for subsoils and values up to ~ 14 for topsoils. Poor correlations for the Harwood Forest organic 0-10 cm soils are also likely to be attributable to higher organic loadings of fresh less decomposed OM and/or insufficient Fe/Al oxides (e.g. for the less organic Cambisols). Extractable OC/Fe_{DCB} ratios calculated for Gleysol and Stagnosol 0-10 cm, 10-20 cm and 20-30 cm soils were highly variable (see Table 3), and ratios calculated for all three soil types are greater (especially in the Gleysol and Stagnosol topsoils) than the maximum sorptive capacity of 0.22 g OC per g Fe for Fe oxide phases at pH 4-7 determined from sorption experiments (Kaiser and Guggenberger 2006). This indicates that these acidic, OM-rich soils contained organo-Fe associations in the form of precipitated complexes and that mechanisms other than simple sorption are responsible for stabilising OC, consistent with previous findings for similar low pH organic soils (Wagai and Mayer 2007; Wagai et al. 2011). Indeed no or negative correlations between Fe_{DCB} and TOC in neutral soils have been explained by the decreased number of positively charged surface hydroxyls (Kögel-Knabner et al. 2008). Kaiser et al. (2011), however, found that positive relationships between oxalate extractable Al and Fe and SOC contents were strongest for near-neutral arable soils rather than acidic forest subsurface soils such as those studied here.

Alongside Fe and Al oxides, other mineral components which contribute to SOM sorption and stabilisation can possibly be removed during the selective dissolution extraction procedures (see Section 3.4.1): oxalate removes Al and Fe in organic complexes (i.e. metal-humus complexes) (Mikutta et al. 2006) and oxalate and DCB dissolve short range order Al silicates (Eusterhues et al. 2005b). Therefore the possible role of other soil components that were extracted alongside Fe/Al oxides and SOM associated with Fe/Al oxides, mainly metal-humus complexes and short range order Al silicates, should be considered. For example, stable OM in acidic soil environments has been found to be predominantly associated with Fe oxides and short-range order Al silicates (Kögel-Knabner et al.

2008). The soils under investigation here were not subjected to pyrophosphate extractions (D'Angelo et al. 2009) or chemical pre-treatments with sodium persulfate ($Na_2S_2O_8$) (Eusterhues et al. 2005b) to selectively remove organic Fe and Al complexes in soil samples prior to oxalate extraction. D'Angelo et al (2009) measured both oxalate and pyrophosphate extractable OC and Fe in a range of agricultural and forest soils and found that pyrophosphate extractable forms of Fe were more important for retaining SOC than oxalate extractable forms of Fe. Overall, the correlation approach does not clarify the role of Fe/Al oxides in preserving OC in these gley soils. The interacting factors mentioned above, along with the possibility that SOC contents varied independently of Fe and Al oxide contents as a result of variable surface loadings of different organic inputs at different soil depths (see Section 4.3), could provide explanations for the lack of correlations observed. However, future work involving particle-size in combination with density fractionation and/or pyrophosphate extractions or chemical pre-treatments to remove organic Fe and Al complexes prior to sequential oxalate and DCB extractions could be useful.

5. Conclusions

This study has confirmed that total Fe oxides (70-90 % of the total Fe present) in the gley 20-30 cm soils of Harwood forest comprised mainly of strongly crystalline Fe oxide phases (50-80 % of total Fe oxides present). Large amounts of SOC were associated with Fe/Al oxides (generally 70-90 % of total SOC) and therefore, as found in previous microanalytical investigations of these soils, these mineral surfaces appear to play a role in stabilising OC in gley soils. Absence of significant differences between SOC storage in the gley soils studied here, however, may be due to hydrological differences not being great enough to differentially affect the development of redoximorphic conditions and therefore contrasting OM enrichment and depletion patterns. Total OC and extractable OC contents were not found to be linearly related to Fe/Al oxide contents for any of the soil profiles and the lack of linear correlations observed is possibly due to a variety of factors including high loadings of fresh less decomposed OM, especially for the organic 0-10 cm soils, and in some cases insufficient amounts of Fe/Al oxides for OM to interact. Also, variable surface loadings of different organic inputs at different soil depths and contributions of organo-Fe associations in the form of precipitated complexes, as indicated by high OC/Fe ratios in these OM-rich acidic soils may contribute to the lack of linear correlation. Furthermore, contributions from other extractable soil components (e.g. Fe- and other

metal-humus complexes, short range order Al silicates) are likely to be important for OM stabilisation. Drawing on statistical test results, significant differences observed suggested that contrasting gley soil hydrological regimes had an effect on total subsoil Fe concentrations, and total and weakly crystalline Al oxide concentrations. Also, significantly different concentrations of strongly crystalline Fe oxides between 10-20 and 20-30 cm Stagnosol soils suggested that the Stagnosols possibly experienced stronger within-profile differences in hydrological conditions and redox oscillations than Gleysols. Geochemical investigations also indicated that mineral phases other than Fe/Al oxides in mineral subsoils preferentially adsorb N-rich microbially processed compounds and that OM associated with weakly and strongly crystalline Fe/Al-oxides in the soils studied had high hydroxyl, aliphatic, carbonyl, aromatic, amide, phenolic, carboxylate and carbohydrate content. Overall this work shows that interactions between Fe/Al oxides and SOM in redox-dynamic gley soils under different hydrological regimes are complex and further investigations of SOC stabilisation in these systems using selective dissolution and other complementary techniques are required.

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Figure captions

Fig. 1 Soil C and N stocks (t ha^{-1}) at different depths in the Harwood forest Gleysols, Stagnosols and Cambisols. Arithmetic mean value ± SD of values acquired from five different soil pit profiles are indicated for Gleysols and Stagnosols.

Fig. 2 FT-IR spectra for oxalate extracts from a) 10-20 cm and b) 20-30 cm Gleysol, Stagnosol and Cambisol Harwood forest soils.

Fig. 3 FT-IR spectra for dithionite-citrate-bicarbonate (DCB) extracts from a) 10-20 cm and b) 20-30 cm Gleysol, Stagnosol and Cambisol Harwood forest soils.

Fig. 4 FT-IR spectra for Harwood forest Gleysol 10-20 cm and 20-30 cm whole soils before extraction.

List of Supplementary Digital Content

Table 1.doc

Figures 1 and 2.doc

Figure 1

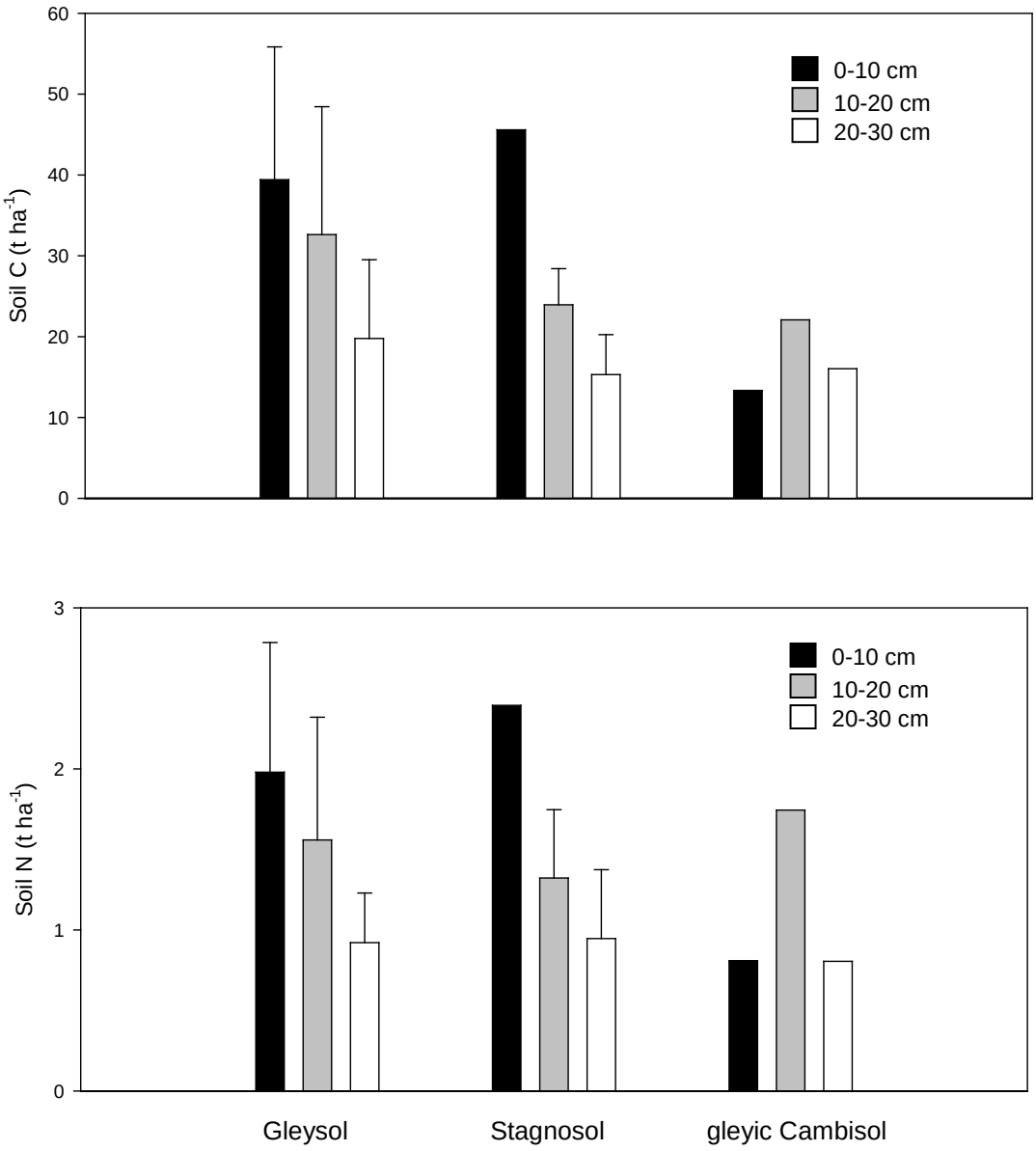
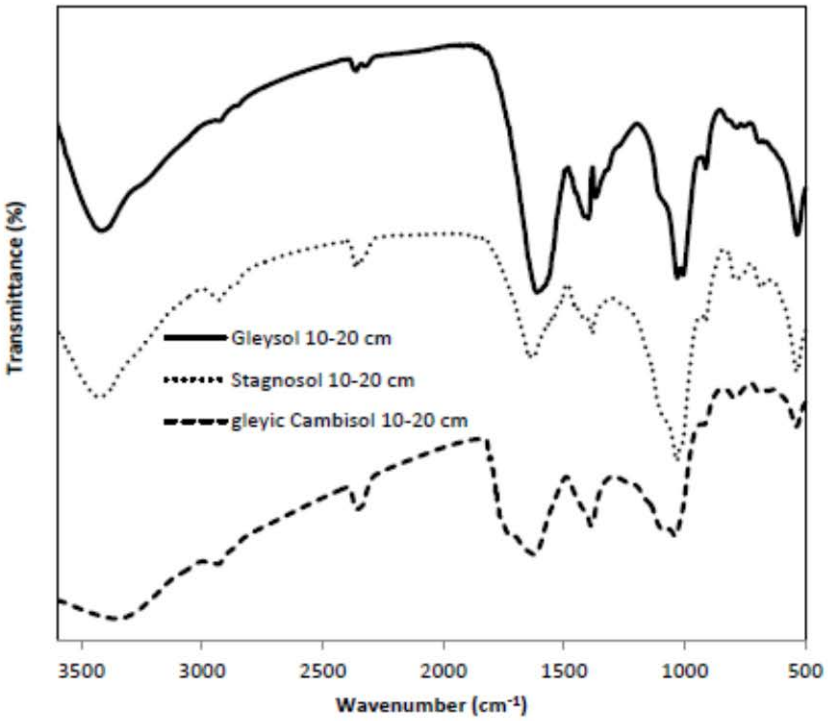

Soil C (t ha-1)
60
50
40
30
20
10
0
0-10 cm
10-20 cm
20-30 cm
Soil N (t ha-1)
3
2
1
0
0-10 cm
10-20 cm
20-30 cm
Gleysol
Stagnosol
gleyic Cambisol

Figure 2

a)


Transmittance (%)
Gleysol 10-20 cm
Stagnosol 10-20 cm
gleyic Cambisol 10-20 cm
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

b)

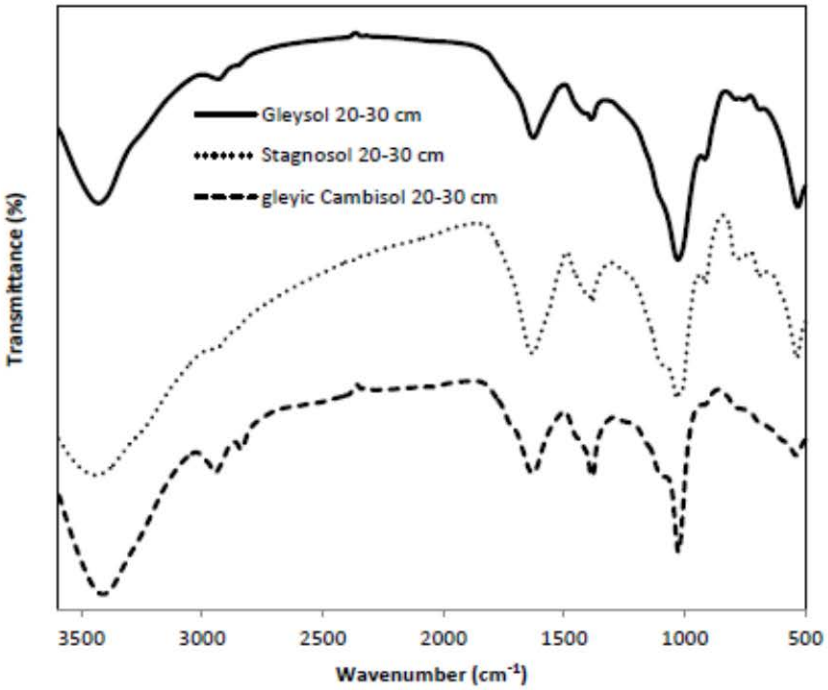
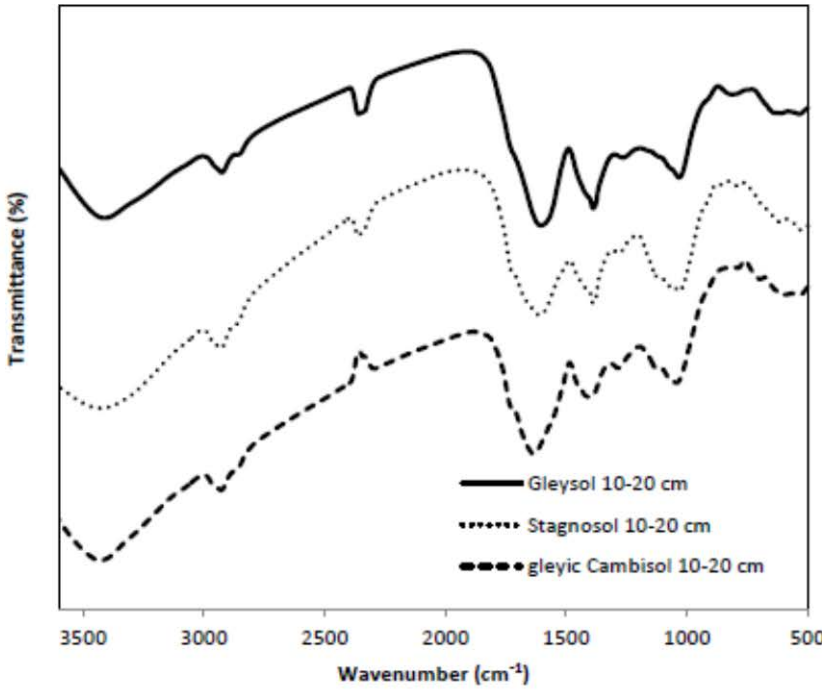

Transmittance (%)
Gleysol 20-30 cm
Stagnosol 20-30 cm
gleyic Cambisol 20-30 cm
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Figure 3

a)


Transmittance (%)
Gleysol 10-20 cm
Stagnosol 10-20 cm
gleyic Cambisol 10-20 cm
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

b)

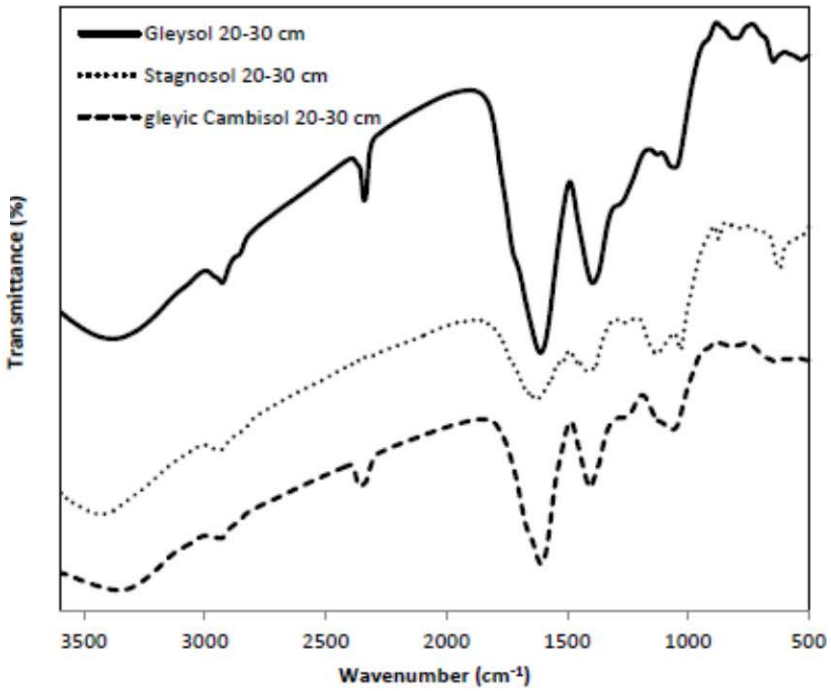

Transmittance (%)
Gleysol 20-30 cm
Stagnosol 20-30 cm
gleyic Cambisol 20-30 cm
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Figure 4

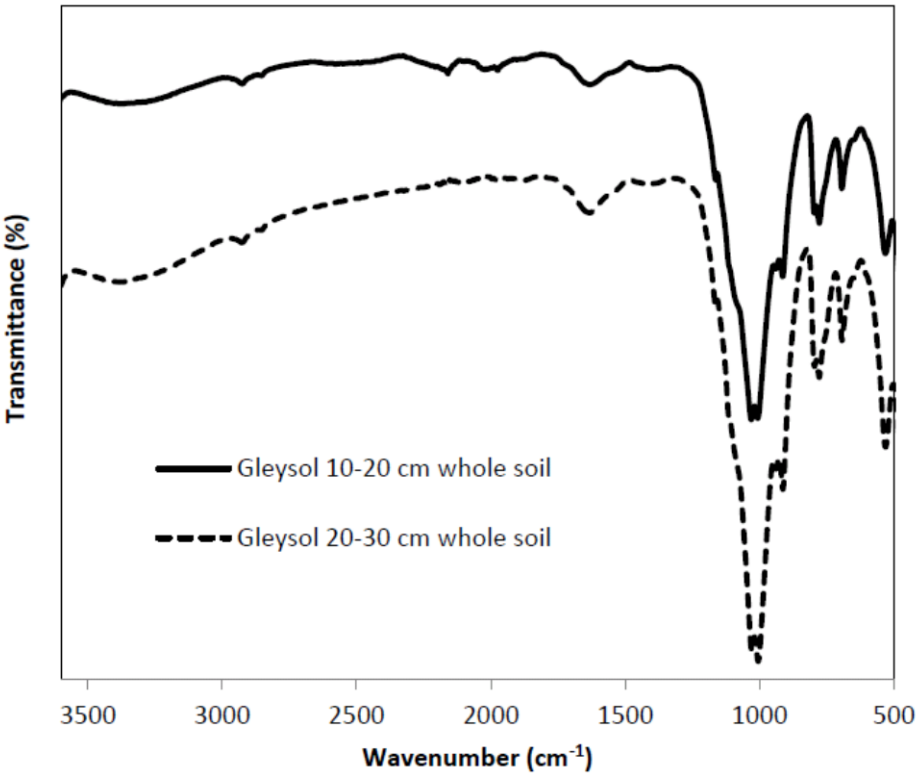

Transmittance (%)
Gleysol 10-20 cm whole soil
Gleysol 20-30 cm whole soil
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Table 1: Soil profile descriptions, physical and chemical characteristics of Harwood forest soils based on the mean of five replicate soil profiles (only one profile for the Cambisol) and three replicate sub-samples for each profile (figures in brackets show one standard deviation).

Soil type (sampling depth (cm))	**Soil horizon (horizon depth (cm))**	**Hydrological regime, elevation and grid reference**	**Visual observations**	**Water content (% of mass)**	**Water-filled pore space (%)**	**Bulk density (g cm^{-3})**	**pH**	**Organic matter content (%)**	**Particle size distribution (%)**			**Texture classification**
									Sand 60-2000 µm	**Silt 2-60 µm**	**Clay < 2 µm**	
Gleysol												
0-10 cm	**Ao 0-10 cm**	Poorly draining, permanent saturation at depth from ground water. *Elevation*: 300 m 55° 14' 49" N, 1° 58' 3" W	Dark brown.	82 (23)[a]	-	0.50 (0.03)[a]	4.1 (0.7)[a]	24 (15)[a]	51[c]	46[c]	3[c]	Sandy loam
10-20 cm	**A 10-20 cm**		Dark greyish brown. Few distinct orange mottles.	37 (4)	60 (48)	0.89 (0.41)	4.5 (1.1)	6.6 (2.0)	53[c]	44[c]	3[c]	Sandy loam
20-30 cm	**Bg 20-35+ cm**		Brownish grey. Frequent orange mottles.	24 (5)	47 (18)	1.39 (0.54)	4.3 (0.5)	4.4 (1.6)	41[c]	52[c]	7[c]	Silt loam
Stagnosol		Poorly draining, upper soil horizons saturated by seasonally perched water table. *Elevation:* 240 m 55° 12' 23" N, 2° 0' 24" W										
0-10 cm	**Ao 0-9 cm**		Blackish grey.	100 (0)	-	0.44 (0.14)[b]	3.9 (0.1)[b]	24 (6)[b]	54[c]	44[c]	2[c]	Sandy loam
10-20 cm	**A(g) 9-20 cm**		Mottled grey. Frequent distinct mottles.	49 (16)	69 (13)	0.95 (0.21)	4.3 (0.4)	9.2 (3.3)	55[c]	42[c]	3[c]	Sandy loam
20-30 cm	**Bg 20-45+ cm**			35 (6)	54 (18)	0.99 (0.17)	4.7 (0.8)	5.3 (1.1)	28[c]	67[c]	5[c]	Silt loam
Cambisol												
0-10 cm	**Ah 0-3 cm and A 3-12 cm**	Freely draining. *Elevation:* 240 m 55° 12' 22" N, 2° 0' 22" W	Dark brown. Brown.	66[c]	-	0.62[c]	5.4[c]	8.5[c]	53[c]	45[c]	2[c]	Sandy loam
10-20 cm	**B(g) 12-32+ cm**		Greyish brown. Indistinct mottles.	66 (30)	82 (9)	1.08 (0.13)	5.3 (0.1)	6.8 (0.1)	64[c]	34[c]	2[c]	Sandy loam
20-30 cm	**B(g)**			45 (0)	68 (6)	0.96 (0.06)	5.1 (0.0)	5.4 (0.3)	72[c c]	27[c]	1[c]	Loamy sand

[a]Values determined as mean of single soil samples from five replicate profiles, [b]values determined as mean of single soil samples from two replicate profiles and [c]values determined for single soil samples from one profile.

Table 2: Soil organic carbon and total N concentrations determined for whole soils and extracted soil residues, corresponding C/N ratios and calculated soil C and N concentrations associated with Fe/Al oxides for Harwood forest soils based on the mean of five replicate soil profiles (only one profile for the Cambisol) and three replicate sub-samples for each profile (figures in brackets show one standard deviation).

Soil type (sampling depth (cm))	**Whole soil OC concentration (%)**	**Soil residue OC concentration after oxalate and DCB extraction (%)**	**Calculated oxalate and DCB extractable SOC concentration (%)** ***[% of total whole soil OC]***	**Whole soil total N concentration (%)**	**Soil residue total N concentration after oxalate and DCB extraction (%)**	**Calculated oxalate and DCB extractable soil N concentration (%)** ***[% of total whole soil N]***	**Whole soil C/N ratio**	**Soil residue C/N ratio after oxalate and DCB extraction**
Gleysol								
0-10 cm	7.9 (3.5) [a]	2.6 (2.8) [a]	5.3 (2.8)[a] *[70 (20)]*	0.40 (0.17)[a]	0.081 (0.053)[a]	0.35 (0.18)[a] *[78 (10)]*	20 (3)[a]	28 (10)[a]
10-20 cm	3.5 (1.0)	0.70 (0.25)	2.8 (0.9) *[79 (7)]*	0.17 (0.03)	0.038 (0.012)	0.13 (0.04) *[76 (11)]*	21 (3)	19 (7)
20-30 cm	1.9 (1.1)	0.41 (0.27)	1.5 (0.8) *[78 (6)]*	0.090 (0.037)	0.025 (0..011)	0.064 (0.032) *[69 (11)]*	21 (3)	17 (7)
Stagnosol								
0-10 cm	10 (3)[b]	5.6 (4.0)[b]	4.5 (1.4)[b] *[48 (27)]*	0.53 (0.13)[b]	0.27 (0.19)[b]	0.26 (0.06)[b] *[53 (25)]*	19 (0)[b]	21 (0)[b]
10-20 cm	2.7 (0.8)	0.46 (0.15)	2.2 (0.8) *[81 (9)]*	0.14 (0.03)	0.041 (0.011)	0.10 (0.03) *[70 (6)]*	18 (3)	12 (3)
20-30 cm	1.5 (0.4)	0.28 (0.10)	1.3 (0.3) *[81 (4)]*	0.093 (0.033)	0.028 (0.009)	0.071 (0.014) *[72 (4)]*	18 (6)	9 (2)
Cambisol								
0-10 cm	2.2[c]	1.7[c]	0.47[c] *[22]*	0.13[c]	0.12[c]	0.014[c] *[11]*	17[c]	14[c]
10-20 cm	2.1 (0.2)	0.32 (0.19)	1.7 (0.4) *[84 (11)]*	0.16 (0.02)	0.026 (0.011)	0.14 (0.03) *[83 (10)]*	13 (1)	12 (3)
20-30 cm	1.7 (0.2)	0.21 (0.07)	1.5 (0.2) *[87 (5)]*	0.083 (0.047)	0.033 (0.024)	0.050 (0.064) *[46 (40)]*	20 (13)	9 (6)

[a]Values determined as mean of single soil samples from five replicate profiles, [b]values determined as mean of single soil samples from two replicate profiles and [c]values determined for single soil samples from one profile.

Table 3. Mean total Al and Fe concentrations (mg g^{-1}), mean oxalate-extractable concentrations of Al (Al_O) and Fe (Fe_O) (mg g^{-1}) and mean total 0.02M oxalate and DCB-extractable Al (Al_{DCB}) and Fe (Fe_{DCB}) concentrations (mg g^{-1}) and oxalate and DCB-extractable OC:Fe_{DCB} ratios for Harwood forest soils. Means are based on the mean of five replicate soil profiles (only one profile for the Cambisol) and three replicate sub-samples for each profile (figures in brackets show one standard deviation).

Soil type (sampling depth (cm))	**Total soil Al concentration (mg g^{-1})**	**Total soil Fe concentration (mg g^{-1})**	**Al_O (mg g^{-1})** ***(0.02 M oxalate)***	**Fe_O (mg g^{-1})** ***(0.02 M oxalate)***	**Al_{DCB} (mg g^{-1})** ***(0.02 M oxalate and DCB) [% of total soil Al]***	**Fe_{DCB} (mg g^{-1})** ***(0.02 M oxalate and DCB) [% of total soil Fe]***	**Extractable OC:Fe_{DCB} ratio (range across Gleysol and Stagnosol profiles)**
Gleysol							
0-10	14 (7) [a]	13 (4) [a]	0.37 (0.06) [a]	1.8 (0.5) [a]	0.97 (0.26) [a] [8.3 ± 3.3]	5.4 (1.3) [a] [43 ± 9]	4 - 22
10-20	19 (4)	17 (7)	0.54 (0.19)	1.6 (0.4)	1.6 (0.4) [8.8 ± 3.3]	16 (7) [66 ± 10]	0.74 – 6.7
20-30	25 (11)	23 (4)	1.1 (0.4)	1.6 (0.4)	2.1 (0.8) [11 ± 6]	16 (6) [66 ± 17]	0.72 – 2.9
Stagnosol							
0-10	15 (4)[b]	12 (6)[b]	0.50 (0.13)[b]	1.6 (0.4)[b]	1.2 (0.1) [b] [7.8 ± 2.7]	8.3 (4.1)[b] [69 ± 0]	3 - 10
10-20	18 (5)	10 (3)	0.44 (0.11)	1.3 (0.1)	0.90 (0.10) [5.4 ± 1.7]	6.8 (2.2) [69 ± 3]	1.1 – 7.1
20-30	11 (4)	11 (4)	0.43 (0.13)	1.2 (0.3)	1.0 (0.2) [11 ± 5]	11 (5) [84 ± 5]	0.27 – 3.0
Gleyic Cambisol							
0-10	16[c]	13[c]	0.27[c]	0.80[c]	0.87[c] [5.4]	8.4[c] [63]	0.56
10-20	15 (2)	13 (1)	0.31 (0.04)	1.0 (02)	1.0 (0.0) [7.0 ± 0.9]	12 (3) [90 ± 17]	1.5
20-30	11 (4)	13 (2)	0.30 (0.01)	0.88 (0.12)	0.87 (0.17) [8.0 ± 4.7]	10 (5) [75 ± 35]	1.7

[a]Values determined as mean of single soil samples from five replicate profiles, [b]values determined as mean of single soil samples from two replicate profiles and [c]values determined for single soil samples from one profile.

Table 4. Total 0.02 M oxalate plus DCB extractable concentrations of Al (Al_{DCB}) and Fe (Fe_{DCB}) (mg g^{-1}), total extractable minus 0.2 M oxalate extractable Fe concentrations (Fe_{DCB-O}) (mg g^{-1}), Fe_O:Fe_{DCB} ratios and $(Fe + Al)_O$ concentrations using 0.2 M oxalate method for selected Harwood forest soil samples (see Supplementary Material Table 1). Gleysol and Stagnosol measurements are the mean of single soil samples from five replicate profiles and Cambisol measurements are values determined for single soil samples from one profile (figures in brackets show one standard deviation).

Soil type (sampling depth (cm))	**Al_{DCB} (0.02 M oxalate and dithioniate extractable Al) (mg g^{-1}) [a]**	**Fe_{DCB} (0.02 M oxalate and dithioniate extractable Fe) (mg g^{-1}) [a]**	**Fe_{DCB-O} (Total extractable Fe minus 0.2 M oxalate extractable Fe) (mg g^{-1})**	**Fe_O:Fe_{DCB} ratio (0.2 M oxalate method)**	**$(Fe + Al)_O$ (mg g^{-1}) (0.2 M oxalate method)**
Gleysol					
10-20	1.4 (0.6)	18 (10)	13 (10)	0.32 (0.14)	5.8 (1.9)
20-30	2.5 (0.9)	19 (10)	16 (11)	0.27 (0.20)	5.2 (1.3)
Stagnosol					
10-20	0.89 (0.04)	7.2 (2.0)	1.5 (0.8)	0.81 (0.09)	6.8 (1.5)
20-30	1.2 (0.20)	15 (6)	9.9 (5.3)	0.37 (0.10)	6.2 (1.5)
Gleyic Cambisol					
10-20	1.0	14	6.4	0.35	8.4
20-30	1.0	13	7.1	0.29	7.0

[a]For direct comparison, values quoted here are different from those in Table 3 because they represent values measured in the samples selected for test extractions.

Table 5. Summary of independent t-test results indicating whether differences in soil measurements at each depth for Gleysols and Stagnosols were statistically significant, where differences were deemed significant if $P \leq 0.05$, s = significant, ns = not significant.

Soil measurement	**Gleysol (n = 5) and Stagnosol (n = 2) Ao 0-10 cm P value**	**Gleysol (n = 5) and Stagnosol (n = 5) A 10-20 cm P value**	**Gleysol (n = 5) and Stagnosol (n = 5) Bg 20-30 cm P value**
Whole SOC concentration (%)	0.475 (ns)	0.174 (ns)	0.500 (ns)
Whole soil total N concentration (%)	0.382 (ns)	0.199 (ns)	0.900 (ns)
Whole soil C/N ratio	0.481 (ns)	0.302 (ns)	0.379 (ns)
Whole SOC stock (t ha^{-1})	0.995 (ns)	0.115 (ns)	0.229 (ns)
Whole soil total N stock (t ha^{-1})	0.744 (ns)	0.645 (ns)	0.172 (ns)
Total soil Al concentration (mg g^{-1})	0.894 (ns)	0.645 (ns)	0.056 (ns)
Total soil Fe concentration (mg g^{-1})	0.860 (ns)	0.128 (ns)	**0.001 (s)**
Al_{DCB} *(0.02 M oxalate and DCB)* (mg g^{-1})	0.221 (ns)	**0.021 (s)**	**0.032 (s)**
Fe_{DCB} *(0.02 M oxalate and DCB)* (mg g^{-1})	0.510 (ns)	0.059 (ns)	0.210 (ns)
Al_O *(0.02 M oxalate)* (mg g^{-1})	0.522 (ns)	0.376 (ns)	**0.022 (s)**
Fe_O *(0.02 M oxalate)* (mg g^{-1})	0.372 (ns)	0.158 (ns)	0.087 (ns)
Fe_{DCB-O} (Total extractable Fe minus 0.2 M oxalate extractable Fe) (mg g^{-1})	-	0.059 (ns)	0.327 (ns)
Fe_O:Fe_{DCB} ratio (0.2 M oxalate method)	-	**0.001 (s)**	0.357 (ns)
$(Fe + Al)_O$ (0.2 M oxalate method) (mg g^{-1})	-	0.380 (ns)	0.308 (ns)
Oxalate and DCB extractable SOC concentration (%)	0.618 (ns)	0.295 (ns)	0.571 (ns)
Oxalate and DCB extractable soil N concentration (%)	0.398 (ns)	0.311 (ns)	0.707 (ns)